



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C11D 3/12, 1/83	A1	(11) International Publication Number: WO 96/18713 (43) International Publication Date: 20 June 1996 (20.06.96)
(21) International Application Number: PCT/US94/14421 (22) International Filing Date: 15 December 1994 (15.12.94) (71) Applicant: ALBEMARLE CORPORATION [US/US]; 451 Florida Street, Baton Rouge, LA 70801-1780 (US). (72) Inventors: HU, Patrick, C.; 6441 Sandstone Avenue, Baton Rouge, LA 70808 (US). LIIMATTA, Eric, W.; 16262 Crepemyrtle Drive, Baton Rouge, LA 70817 (US). (74) Agent: PIPPENGER, Philip, M.; Albemarle Corporation, Patent and Trademark Division, 451 Florida Street, Baton Rouge, LA 70801-1780 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: LIQUID LAUNDRY DETERGENT (57) Abstract Stable zeolite-containing liquid detergents requiring no viscosity-reducing polymer in order to have a viscosity ≤ 1000 mPa.s are aqueous surfactant-structured detergents comprising (A) 5-45 % by weight of suspended zeolite particles, (B) 10-30 % by weight of an alkylbenzene sulfonate/nonionic surfactant admixture in which (1) the nonionic component of the admixture is an ethoxylate of an alcohol or an alkylphenol or a mixture thereof with an amine oxide, (2) the alkylbenzene sulfonate/nonionic surfactant weight ratio is in the range of ~ 0.5 -10/1, (3) the amine oxide/ethoxylate weight ratio is in the range of 0-4/1, and (4) the amine oxide/alkylbenzene sulfonate weight ratio is in the range of 0-0.5/1, (C) an amount of auxiliary builder in the range of 0.5-4.5 % by weight such that the nonionic surfactant/auxiliary builder weight ratio is not higher than ~ 3.5 /1, and (D) 35-80 % by weight of water.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

LIQUID LAUNDRY DETERGENT

Field of Invention

This invention relates to liquid laundry detergents and more particularly relates to such detergents containing zeolite builders.

5 Background

It is known that zeolites have been successfully employed as builders in laundry detergents; and U.S. Patent 4,605,509 (Corkill et al.) discloses commercially attractive detergent powders comprising 5-95% by weight of one or more water-soluble organic surfactants, 5-95% by weight of a zeolite builder, and 5-50% by weight of one or more
10 auxiliary builders.

Developing liquid detergents comparable to the detergent powders of Corkill et al. would be desirable. However, in order for them to be commercially attractive, it would be necessary for these liquid detergents to have the zeolite stably suspended therein and to have a maximum viscosity of 1000 mPa·s, measured at a shear rate of 21 s⁻¹.

15 U.S. Patent 5,252,244 (Beaujean et al.) teaches aqueous zeolite-containing liquid detergents which are stabilized with an electrolyte system comprising at least one carbonate and at least one sulfate and which have viscosities of 2000-11,000 mPa·s (Brookfield viscosimeter, spindle No. 6, 10 rpm).

As taught in U.S. Patent 5,006,273 (Machin et al.), surfactant structuring — believed
20 to consist of an onion-like configuration comprising concentric bilayers of surfactant molecules having water trapped therebetween — permits solid material to be stably suspended in a liquid detergent. However, surfactant systems such as those of Corkill et al. are frequently incapable of producing a structuring phase for a liquid detergent. Moreover, as disclosed by Machin et al., even surfactant systems suitable for this purpose
25 can create another problem when used in an amount such as to provide a surfactant content of at least 10% by weight: Liquid detergents containing such larger amounts of surfactant and suspended solids are apt to have viscosities considerably greater than 1000 mPa·s unless they also contain a viscosity-reducing polymer.

In developing Corkill-like liquid detergents having the characteristics mentioned

above, i.e., stable suspension of the zeolite and a maximum viscosity of 1000 mPa·s, it would be advantageous to be able to avoid having to employ a viscosity-reducing polymer in order to make the detergent pourable; and it would also be desirable for these liquid detergents to contain less auxiliary builder than the Corkill et al. powders. Having a lower
5 auxiliary builder content would reduce the corrosivity of the detergents, lessen detriment to the environment when ecologically-undesirable auxiliary builders are employed, and provide a lower viscosity at any given zeolite level.

Summary of Invention

It has been found that liquid detergents comprising a stable aqueous suspension
10 of zeolite particles and having an auxiliary builder content of <5% by weight and a viscosity of ≤ 1000 mPa·s can be obtained without the use of a viscosity-reducing polymer when they contain certain alkylbenzene sulfonate/nonionic ethoxylate mixtures as the surfactants.

Thus, the invention resides in an aqueous surfactant-structured liquid detergent
15 comprising:

- (A) 5-45% by weight of suspended zeolite particles,
- (B) 10-30% by weight of an alkylbenzene sulfonate/nonionic surfactant admixture in which (1) the nonionic component of the admixture is an ethoxylate of an alcohol or an alkylphenol or a mixture thereof
20 with an amine oxide, (2) the alkylbenzene sulfonate/nonionic surfactant weight ratio is in the range of ~ 0.5 -10/1, (3) the amine oxide/ethoxylate weight ratio is in the range of 0-4/1, and (4) the amine oxide/alkylbenzene sulfonate weight ratio is in the range of 0-0.5/1,
- 25 (C) an amount of auxiliary builder in the range of 0.5-4.5% by weight such that the nonionic surfactant/auxiliary builder weight ratio is not higher than ~ 3.5 /1, and
- (D) 35-80% by weight of water.

Detailed Description

Like the liquid detergents of Machin et al. (the teachings of which are incorporated herein by reference), the detergent compositions of the invention are aqueous surfactant-structured liquid detergents. However, unlike those known liquid detergents, they have the advantages of requiring no viscosity-reducing polymer in order to have a viscosity of
5 ≤ 1000 mPa·s and of being able to have a suspended particle content as high as 45% by weight — a benefit because of the contribution of zeolite to the cleaning ability of a detergent.

The alkylbenzene sulfonate used as a component of the surfactant system may be any of the alkylbenzene sulfonates known to be useful as surfactants. However, it is
10 preferably a salt, usually a sodium salt, of an alkylbenzene sulfonate in which the alkyl group contains 10-15, most preferably 11-12 carbons.

As already mentioned, the ethoxylate utilized together with the alkylbenzene sulfonate to provide the surfactant mixture of the novel compositions may be an ethoxylate of an alcohol or an alkylphenol. Such surfactants are well known and are compounds which
15 usually contain alkyl groups of 8-24 carbons and 4-30 ethoxy groups. Among the ethoxylates which have been found to be particularly useful in the practice of the invention are the C_8 - C_{16} alcohol ethoxylates containing 4-12 ethoxy (EO) groups per molecule and the octylphenol and nonylphenol ethoxylates containing 6-15 EO groups per molecule. The ethoxylates of alkylphenols are apt to be preferred when it is important to keep the
20 auxiliary builder content of the compositions particularly low.

The optional amine oxide component of the surfactant may be any of the amine oxides conventionally employed as surfactants, typically an amine oxide corresponding to the formula $RR'R''NO$ in which R is a primary alkyl group containing 8-24 carbons; R' is methyl, ethyl, or 2-hydroxyethyl; and R'' is independently selected from methyl,
25 ethyl, 2-hydroxyethyl, and primary alkyl groups containing 8-24 carbons. Such amine oxides include, e.g., N-octyldimethylamine oxide, N,N-didecylmethylamine oxide, N-decyl-N-dodecylethylamine oxide, N-dodecyldimethylamine oxide, N-tetradecyldimethylamine oxide, N-tetradecyl-N-ethylmethylamine oxide, N-tetradecyl-N-ethyl-2-hydroxyethylamine oxide, N-hexadecyldimethylamine oxide, N-octadecyldimethylamine oxide, N,N-dieicosylethylamine oxide, N-docosyldimethylamine oxide, N-tetracosyldimethylamine
30 oxide, and mixtures thereof — the preferred amine oxides usually being those containing

one long-chain alkyl group, e.g., N-tetradecyldimethylamine oxide.

When used, the amine oxide may constitute up to 80% of the weight of the nonionic component of the surfactant as long as its concentration is not high enough to provide an amine oxide/alkylbenzene sulfonate weight ratio $>0.5/1$.

5 The alkylbenzene sulfonate/nonionic surfactant proportions required to provide surfactant structuring of the liquid detergents can vary with the particular auxiliary builder employed and with the concentrations of surfactant and auxiliary builder in the compositions — larger amounts of alkylbenzene sulfonate in the mixtures being utilizable when the compositions have the higher surfactant contents, lower alkylbenzene sulfonate/nonionic
10 surfactant ratios being permissible when the detergents have the higher auxiliary builder contents, and the range of useful sulfonate/nonionic surfactant ratios being narrowest at the lowest levels of auxiliary builder. However, in general, the utilizable alkylbenzene sulfonate/nonionic surfactant weight ratios are in the range of ~ 0.5 - $10/1$, preferably ~ 0.8 - $5.3/1$, more preferably ~ 1.5 - $4/1$, and the ratios best suited for particular compositions
15 within the scope of the invention are easily determined by routine experimentation.

As in Corkill et al. (the teachings of which are incorporated herein by reference), the auxiliary builder may be any of the water-soluble inorganic and organic salts conventionally used in detergent compositions to aid the builder in sequestering "hardness" ions, such as calcium and magnesium ions. Exemplary of such salts are the alkali metal
20 (e.g., sodium and potassium) carbonates, bicarbonates, silicates, chlorides, iodides, citrates, phosphates, pyrophosphates, phosphonates, nitrilotriacetates, polyacrylates, polyaspartates, polycarboxylates, and succinates.

Although, as indicated above, the amount of auxiliary builder used in the compositions may vary from 0.5-4.5% by weight, the quantity that is preferred in any
25 given instance depends on factors such as the particular surfactant mixture with which it is utilized, the surfactant content of the composition, and the degree to which the auxiliary builder might adversely affect the environment. Larger amounts of auxiliary builder are needed when the compositions have the lower surfactant contents, and it appears to be important to employ sufficient auxiliary builder to prevent the nonionic surfactant/auxiliary
30 builder weight ratio from exceeding $\sim 3.5/1$. However, it is generally preferred to utilize the smaller amounts of auxiliary builder (i.e., 0.5-3.5% by weight) in combination with

the higher surfactant contents (i.e., 20-30% by weight) to reduce the corrosivity of the detergents, lessen detriment to the environment when ecologically-undesirable auxiliary builders are employed, and provide a lower viscosity at any given zeolite level.

5 The particular zeolite employed as a builder in the novel liquid detergents is not critical as long as it is a particulate sodium salt. Thus, although it may be a zeolite of Corkill et al., other zeolites are also utilizable. It is usually a zeolite A or X or mixture thereof, preferably zeolite A or a zeolite A/zeolite X blend.

10 In the preparation of the liquid detergents of the invention, it is not critical to combine the ingredients in any particular order. However, it is ordinarily preferred to dissolve the water-soluble surfactant mixture and auxiliary builder in water to provide the structuring phase before suspending the zeolite particles therein.

15 The invention is advantageous in its provision of all of its surfactant-structured liquid detergents, but it is particularly beneficial in its permitting the formation of the detergents having surfactant contents of 20-30% and zeolite contents of 15-45% — i.e., those having a compositional makeup which has previously necessitated the use of viscosity-reducing polymers to make them pourable. The liquid detergents of the invention may include minor amounts of additives, such as the dyes, perfumes, enzymes, and preservatives frequently used in such compositions; and they could also include the viscosity-reducing polymers of known liquid detergents without losing their surfactant structuring. However, it is
20 unlikely that it would ever be really desirable to incorporate viscosity-reducing polymers: They would be unnecessary and therefore would merely add to the cost of the detergents.

25 The following examples are given to illustrate the invention and are not intended as a limitation thereof. Unless otherwise specified, quantities mentioned in the examples are quantities by weight, and codes are used to represent detergent ingredients as indicated below.

Code	Ingredient
S-1	Sodium citrate
S-2	Sodium carbonate
LAS	Sodium dodecylbenzene sulfonate
AS	Sodium C ₁₂ -C ₁₅ alkyl sulfate
AES	Sodium lauryl ether sulfate containing three EO (-OCH ₂ CH ₂ -) groups per molecule
AE	A 7-EO ethoxylate of a mixture of C ₁₂ -C ₁₄ alcohols
NPE	The 9-EO ethoxylate of nonylphenol

EXAMPLE 1

Prepare a series of base compositions to determine their ability to serve as the structuring phases of zeolite-containing liquid detergents. The ingredients used and the amounts employed are shown in Table I.

TABLE I								
Composition	LAS	AS	AES	AE	NPE	S-1	S-2	Water
A	7	--	--	3	--	5	--	85
B	14	--	--	6	--	4	--	76
B-1	--	14	--	6	--	4	--	76
B-2	--	--	14	6	--	4	--	76
C	14	--	--	6	--	7	--	73
C-1	--	14	--	6	--	7	--	73
C-2	--	--	14	6	--	7	--	73
D	14	--	--	--	6	3	--	77
E	14	--	--	--	6	5	--	75
E-1	--	14	--	--	6	5	--	75
E-2	--	--	14	--	6	5	--	75
F	14	--	--	--	6	7	--	73
F-1	--	14	--	--	6	7	--	73
F-2	--	--	14	--	6	7	--	73

TABLE I (continued)								
G	18	--	--	12	--	--	4.1	65.9
H-1	8	--	--	12	--	5	--	75
H-2	--	8	--	12	--	5	--	75
H-3	--	--	8	12	--	5	--	75
I-1	8	--	--	--	12	6	--	74
I-2	--	8	--	--	12	6	--	74
I-3	--	--	8	--	12	6	--	74

EXAMPLE 2

Test each of the base compositions of Example 1 for ability to serve as a structuring phase by (1) stirring zeolite particles therein to form a suspension containing 10-15% by weight of suspended zeolite, (2) storing the suspension at room temperature, and (3) examining the suspension after two months to determine its stability. The test shows that each of the suspensions made from a base composition within the scope of the invention (i.e., the compositions having an alphabetic designation with no numeric suffix) is stable, whereas there is appreciable settling of the zeolite from each of the comparative base compositions to form a second phase.

As demonstrated above, the use of selected alkylbenzene sulfonate/nonionic ethoxylate mixtures as the surfactants has the unexpected result of providing a surfactant structuring of zeolite-containing liquid detergents that is not obtained when they are replaced with surfactant mixtures which are normally considered equivalent thereto. This phenomenon is also observed when a portion of the ethoxylate is replaced with an amine oxide and/or larger amounts of zeolite are suspended in the base compositions to form other liquid detergents having viscosities ≤ 1000 mPa·s and zeolite contents as high as 45% by weight.

WHAT IS CLAIMED IS:

1. An aqueous surfactant-structured liquid detergent comprising (A) 5-45% by weight of suspended zeolite particles, (B) 10-30% by weight of an alkylbenzene sulfonate/nonionic surfactant admixture in which (1) the nonionic component of the admixture is an ethoxylate of an alcohol or an alkylphenol or a mixture thereof with an amine oxide, (2) the alkylbenzene sulfonate/nonionic surfactant weight ratio is in the range of ~0.5-10/1, (3) the amine oxide/ethoxylate weight ratio is in the range of 0-4/1, and (4) the amine oxide/alkylbenzene sulfonate weight ratio is in the range of 0-0.5/1, (C) an amount of auxiliary builder in the range of 0.5-4.5% by weight such that the nonionic surfactant/auxiliary builder weight ratio is not higher than ~3.5/1, and (D) 35-80% by weight of water.
2. The liquid detergent of claim 1 having a viscosity ≤ 1000 mPa·s.
3. The liquid detergent of claim 1 wherein the alkylbenzene sulfonate/nonionic surfactant weight ratio is in the range of ~1.5-4/1.
4. The liquid detergent of claim 1 wherein the alkylbenzene sulfonate is a salt of an alkylbenzene sulfonate in which the alkyl group contains 10-15 carbons.
5. The liquid detergent of claim 4 wherein the alkylbenzene sulfonate is a sodium salt of an alkylbenzene sulfonate in which the alkyl group contains 11-12 carbons.
6. The liquid detergent of claim 1 wherein the ethoxylate contains 4-30 ethoxy groups and is an ethoxylate of one or more alcohols containing 8-24 carbons.
7. The liquid detergent of claim 6 wherein the ethoxylate is a C_8 - C_{16} alcohol ethoxylate containing 4-12 ethoxy groups per molecule.
8. The liquid detergent of claim 1 wherein the ethoxylate contains 4-30 ethoxy

groups and is an ethoxylate of an alkylphenol in which the alkyl group contains 8-24 carbons.

9. The liquid detergent of claim 8 wherein the ethoxylate is an octylphenol or nonylphenol ethoxylate containing 6-15 ethoxy groups per molecule.

10. The liquid detergent of claim 1 wherein the ethoxylate is the sole nonionic component of the surfactant admixture.

11. The liquid detergent of claim 1 wherein the nonionic component of the surfactant admixture is a mixture of the ethoxylate and an amine oxide.

12. The liquid detergent of claim 11 wherein the amine oxide is a compound corresponding to the formula $RR'R''NO$ in which R is a primary alkyl group containing 8-24 carbons; R' is methyl, ethyl, or 2-hydroxyethyl; and R'' is independently selected from methyl, ethyl, 2-hydroxyethyl, and primary alkyl groups containing 8-24 carbons.

13. The liquid detergent of claim 1 wherein the auxiliary builder is sodium citrate.

14. The liquid detergent of claim 13 having a viscosity ≤ 1000 mPa·s, a suspended zeolite content of 15-45% by weight, a surfactant mixture content of 20-30% by weight, an alkylbenzene sulfonate/nonionic surfactant weight ratio in the range of $\sim 1.5-4/1$, and a sodium citrate content of 0.5-3.5% by weight.

15. The liquid detergent of claim 14 wherein the surfactant is a mixture of (A) a sodium salt of an alkylbenzene sulfonate in which the alkyl group contains 11-12 carbons and (B) an octylphenol or nonylphenol ethoxylate containing 6-15 ethoxy groups per molecule.

16. The liquid detergent of claim 1 wherein the auxiliary builder is sodium carbonate.

17. The liquid detergent of claim 16 having a viscosity ≤ 1000 mPa·s, a suspended zeolite content of 15-45% by weight, a surfactant mixture content of 20-30% by weight, an alkylbenzene sulfonate/nonionic surfactant weight ratio in the range of ~1.5-4/1, and a sodium carbonate content of 0.5-3.5% by weight.

18. The liquid detergent of claim 17 wherein the surfactant is a mixture of (A) a sodium salt of an alkylbenzene sulfonate in which the alkyl group contains 11-12 carbons and (B) an octylphenol or nonylphenol ethoxylate containing 6-15 ethoxy groups per molecule.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/12 C11D1/83

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RESEARCH DISCLOSURE, no. 359, March 1994 HAVANT GB, pages 151-6, XP 000440544 NOVO NORDISK see page 153; example 6	1,3,6,7
A	---	13
X	EP,A,0 530 708 (ALBRIGHT & WILSON) 10 March 1993 see examples 14,15	1,3,4, 13,16
A	---	1
	EP,A,0 436 240 (UNILEVER) 10 July 1991 see page 3, line 43 - line 47; claims 1,7 ---	
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

13 March 1996

Date of mailing of the international search report

27.03.1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Van Bellingen, I

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 9125 Derwent Publications Ltd., London, GB; AN 91-181526 & JP,A,03 109 500 (LION) , 9 May 1991 see abstract	1
A	--- EP,A,0 295 021 (ALBRIGHT & WILSON) 14 December 1988 see claim 6; table 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 94/14421

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-530708	10-03-93	AU-B- 665766	18-01-96
		AU-B- 2133092	11-03-93
		BG-A- 96827	24-03-94
		CA-A- 2077253	01-03-93
		CN-A- 1073973	07-07-93
		GB-A, B 2259519	17-03-93
		JP-A- 5209198	20-08-93
		NZ-A- 244159	22-12-94
		ZA-A- 9206551	08-06-93
EP-A-436240	10-07-91	US-A- 5324455	28-06-94
EP-A-295021	14-12-88	AU-B- 1754388	15-12-88
		BG-A- 47649	15-08-90
		GB-A- 2205852	21-12-88
		IN-A- 172745	20-11-93
		JP-A- 1004700	09-01-89
		OA-A- 8905	31-10-89